

CLAIMS

We claim:

1. A biocompatible, biodegradable, macromolecular water-absorbent hybrid material (WAHM), having a three-dimensional configuration with intermolecular covalent bonds and containing free functional groups selected from OH, SH, NH₂ and COOH, said polymer being formed by polymer-polymer intercoupling reaction between a natural water-soluble polymer A or its derivatives having a molecular weight between 20,000 and 300,000Da , and a synthetic polymer B in an adequate ratio between 1 and 50% from dried mixture (A+B), wherein the natural polymer A is selected from:

amphoteric reactants, partially denatured or chemically modified natural polymer, that dissociates in water to form both anions and cations, and which can undergo polymer-polymer intercoupling reactions,

and wherein:

synthetic polymer B is a linear or branched reactive synthetic copolymer having a molecular weight of 50,000 – 500,000Da derived from a vinyl monomer and an ethylenically unsaturated monomer, said copolymer having a backbone with polymeric subunits R_n and R_r, wherein R represents a subunit covalently bonded to the polymer backbone, n represents non-reactive chemical functional groups and r represents reactive chemical functional groups.

2. A polymeric material as in Claim 1, wherein the natural polymer forming in water anions and cations (COO⁻ and NH₃⁺) with at least 1×10^{-3} moles COOH/g and at least 0.5×10^{-3} moles NH₂/g with an isoelectric point (IEP) not less than 2.5 and not more than 10.5.

3. A polymeric material as in Claim 1, wherein the natural polymer is selected from proteins of animal, vegetal or bacterial origins and their derivatives.

4. A polymeric material as in Claim 1, wherein the natural polymer is selected from: collagen, collagenic biopolymers (atelocollagen, solubilized collagen, gelatin and collagen hydrolysate) proceed from terrestrial and marine resources and derivatives of those, -alfa-keratose, gama-keratose, keratin hydrolysate and derivatives , elastin and derivatives , fibrin and derivatives,

fibroin and derivatives, ovalbumine, bovine serumalbumine and albumine derivatives, casein and its derivatives, soybean protein and its derivatives.

5. A polymeric material as in Claim 1, wherein the natural polymer is gelatin (food grade or pharmaceutical grade), obtained from specific resources (hides, tendons and other conjunctive tissues' type).

6. A polymeric material as in Claim 1, wherein the natural polymer is chemically modified by acylation reaction using a modifying agent, such as a carbonyl compound selected from anhydrides (phthalic anhydride; ; maleic anhydride ; citraconic anhydride; itaconic anhydride and succinic anhydride) and acid chlorides (benzoyl chloride, benzenesulfonyl chloride and butyrylchloride).

7. A polymeric material as in Claim 6, wherein the natural polymer is chemically modified by using a modifying agent with chemical functions' content not less than 1×10^{-5} moles/g and not more than 1×10^{-2} moles/g, such as between 1×10^{-4} moles/g and 1×10^{-3} moles/g.

8. A polymeric material as in Claim 1, wherein the polymer B is a linear or branched polymer obtained by a single stage polyreaction such as polymerization or polycondensation or in two stages, by a polyreaction followed by chemical modification such as polymer-analogous transformations.

9. A polymeric material as in Claim 8, wherein R includes a reactive R_r or non-reactive R_n chemical function.

10. A polymeric material as in Claim 8, wherein R includes a spacer group interposed between the chemical function and the chain that is anchored to it.

11. A polymeric material as in Claim 10 wherein the spacer group is selected from $-\text{CO}-\text{O}-$ and $-(\text{CH}_2)_n-$ with n equals 1- 4.

12. A polymeric material as in Claim 1, wherein the reactive chemical functions of synthetic polymer B, are ionic reactive chemical functions R_r selected from $-\text{CO}-\text{O}-\text{CO}-$ and $-\text{CO}-\text{NH}-\text{CO}-$.
13. A polymeric material as in Claim 12, wherein the reactive chemical function is selected from maleic anhydride, itaconic anhydride, citraconic anhydride, 2-octenylsuccinic anhydride and corresponding imides.
14. A polymeric material as in Claim 1, wherein the ionic reactive chemical functionality of polymer B, is symbolized as f_r^B , and is not less than 5×10^{-3} moles "r"/g and not more than 1×10^{-2} moles "r"/g.
15. A polymeric material as in Claim 1, wherein the non-reactive chemical functions R_n can comprise m number of groups ($m=1-4$) selected from hydrogen, aliphatic or aromatic hydrocarbon residues with 1 to 20 carbon atoms, non-active ester, ether, or imino groups or non-active halogen derivatives.
16. A polymeric material as in Claim 15, wherein the non-reactive chemical functions R_n may partially include polar chemical groups selected from hydroxyl, amino, amido or carboxylic groups.
17. A polymeric material as in Claim 15, wherein the non-reactive substituents of the polymer B, are attached to the backbone of the copolymer, that represents monomer residues.
18. A polymeric material as in Claim 15, wherein the synthetic polymer B is prepared from monomers with non-reactive groups, selected from
styrene, alpha - methylstyrene and alkylated styrenes such as ethylstyrene or tert-butylstyrene, vinyl-toluene, vinyl esters of saturated C_1-C_4 -carboxylic acids such as vinyl formate, vinyl acetate or vinyl propionate, alkyl vinyl ethers with at least 2 carbon atoms in the alkyl group, such as ethyl vinyl ether or butyl vinyl ether, acrylate or methacrylate esters such as

2-ethylhexyl acrylate, n-butyl acrylate, isobutyl acrylate, t-butyl acrylate, hexyl acrylate, n-butyl methacrylate, lauryl methacrylate and isodecyl methacrylate; conjugated diolefins such as butadiene, isoprene, and piperylene; allenes such as allene, methyl allene and chloroallene; olefin halides such as vinyl chloride, vinyl fluoride and polyfluoro-olefins, ethylene, propene, isobutylene, butadiene, isoprene, esters of monoethylenically unsaturated $C_3 - C_6$ -carboxylic acids, i.e. esters of monohydric C_1-C_8 - alcohols and acrylic acid, methacrylic acid or maleic acid, monoesters of maleic acid, i.e. monomethyl maleate, and hydroxyalkyl esters of said monoethylenically unsaturated carboxylic acids, i.e. 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl methacrylate, N-vinyl lactams such as N-vinylpyrrolidone or N-vinylcaprolactam, acrylic and methacrylic esters of alkoxyated monohydric saturated alcohols, vinyl pyridine and vinyl morpholine, N- vinylformamide, dialkyldiallylammonium halides such as dimethyldiallylammonium chloride, diethyldiallylammonium chloride, allylpiperidinium bromide, N-vinylimidazoles such as N-vinylimidazole, 1-vinyl-2-methylimidazole and N-vinylimidazolines such as N-vinylimidazoline, 1-vinyl-2-methylimidazoline, 1-vinyl-2-ethylimidazoline or 1-vinyl-2-propylimidazoline, acrylamide, methacrylamide or acrylonitrile.

19. A polymeric material as in Claim 15, wherein the synthetic polymer B is prepared from ethylene, propene, styrene, isobutylene, vinyl acetate, methyl acrylate, methyl methacrylate, acrylamide, vinyl ether, N-vinylpyrrolidone, acrylic acid, methacrylic acid or maleic acid.

20. A polymeric material as in Claim 15, wherein the synthetic polymer B is prepared from pharmaceutically accepted monomers selected from poly (ethylene-alt-maleic anhydride), poly(ethylene-graft-maleic anhydride), poly(isobutylene-co-maleic anhydride), poly(isoprene - graft-maleic anhydride), poly(maleic anhydride - co - 1-octadecene), poly(propylene-graft - maleic anhydride), poly(styrene-co-maleic anhydride).

21. A process for preparing a biocompatible, biodegradable, macromolecular water-absorbent hybrid material as in Claim 1, comprising reacting a natural polymer A with a polymer B by intercoupling in water in the absence of a cross linking or coupling agent.

22. A process as in Claim 23, comprising reacting reactants as solutions or suspensions, for their preparing has been exclusively used water, by intercoupling in water.

23. A process as in Claim 23, as exemplified for a system formed from two reactants, by symbolic chemical equation of Figure 1.

24. A process for preparing a biocompatible, biodegradable, macromolecular water-absorbent hybrid material as in Claim 1 comprising the following steps :

- i. preparing a suitable amount of solid natural polymer A, referred to as reactant R1, dissolving it in a volume of water with conductivity less than $10\mu\text{S}$ and temperature of 60°C , by mixing the two components in adequate ratios to obtain solutions with concentration not less than 1% and not more than 20%, such as between 2% and 10%;

b. preparing a quantity of solid reactive polymer B, as powder or granules, suspending in water with conductivity less than $10\mu\text{S}$, by simply mixing the two components in adequate ratio to obtain a solid-liquid dispersion (WD-1) with a concentration in solid not less than 5% and not more than 35%, such as between 15% and 25%;

The water dispersion of reactive polymer B, WD-1, is stirred 0.5 hours at room temperature .

In the end, the solid phase is separated by filtration at vacuum. The wet solid (WS) is washed for 3 times with a quantity of water, which represents a mass of 3 to 5 times higher than the initial quantity of reactive polymer B used for its preparation.

These solid, obtained after washing and filtration, is introduced in a blender and then is added a quantity of water, obtaining a new solid –liquid aqueous dispersion (WD-2) with a concentration in solid not less than 20% and not more than 50% , such as between 30% and 40%.

The water dispersion WD-2 is mixed at room temperature not less than 5 minutes and not more than 25 minutes, preferably between 10 and 20 minutes, at a speed not less than 1000 rpm and not more than 5000 rpm, preferably between 2500 rpm and 3500 rpm. The resultant aqueous dispersion, that contains reactive polymer B , being represented as R2.

c. preparing a suitable amount of substances with basic character selected from : lithium hydroxide, sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium carbonate, lithium bicarbonate, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate and ammonium bicarbonate (their use is individually or preferable in mixture), referred to as reactant R3, dissolving in a volume of water with conductivity less than $10\mu\text{S}$, by a simple mixing of the two components, in adequate ratios so to obtain solutions of concentration not less than 5% and not more than 35%, preferably between 10 and 20% .

d. polymer-polymer intercoupling reaction consist from:

In a dual-shaft jacketed kneader reactor, with a speed ratio between stirrer and shaft $n_1 : n_2$ not less than 1:1.05 and not more than 1:1.4, preferably between 1:1.1 and 1:1.2, with a slow speed of rotor (1) not less than 20 rpm and not more than 250 rpm, preferably between 60rpm and 120rpm, equipped with a heating-cooling jacket and thermometer, are introduced first the reactant R2.

Then under mixture is added the whole quantity of reactant R1 in adequate ratio so to represent not less than 1% and not more than 99% from the mixture in dry state formed from polymer A and polymer B, preferably between 5% and 35%.

The mixture of reactant R1 and reactant R2 is mixed not less than 10 minutes and not more than 40 minutes, preferably between 15 minutes and 25minutes, at a temperature not less than 15°C and not more than 75°C , preferably between 35°C and 55°C .

Then is added the whole quantity of reactant R3 in adequate ratio that not be less than 1% and not more than 25% , preferably between 5% and 20% of dried base based on dried mixture of polymer A and polymer B.

The mixing continues not less than 1 hour and not more than 12 hours, preferably between 3 hours and 8 hours, at temperature of reaction mass before the reactant R3 was added.

e. reaction mass processing consist from:

The reaction mass obtained in kneader is profiling with screw extruder, as a bundle of rods with 40...100 mm in diameter.

The hydrogel rods are laid on metallic framework covered with screen from polyester with mesh of 250 microns. The frameworks are introduced in a circulating warm air oven for drying the hydrogel by evaporation.

The water evaporation occurs in warm-air current at a temperature not less than 40°C and not more than 100°C, preferably between 50°C and 90°C and a speed of air circulation of 0.5-1.5 m/s. The water evaporation process (drying) is ended when the solid mass as rods type achieve a humidity content not less than 3% and not more than 15% , preferably between 7% and 12%.

The mass of rods that come out of oven is grinded with a mill with cones, adjusted to obtain granules with equivalent diameter of particles included between 150 microns and 2500 microns.

After , the granular mass is cooled at ambient temperature, is collected in polyethylene bags and is deposited in conditioning rooms with air circulation at temperature of $25 \pm 5^\circ\text{C}$ and relative humidity of $55 \pm 10\%$, for a period of time not less than 24 hours and not more than 96 hours, preferably between 48 hours and 72 hours.

Finally, the conditioned granular mass, representing water absorbent hybrid material (WAHM), is packed in polyethylene bags, that after their filling are closed by sealing.

25. A chemical process in water for preparing a biocompatible, biodegradable, water-absorbent hybrid material as in Claim 1, is illustrated by the model from scheme 2.

26. A biocompatible, biodegradable, water-absorbent hybrid material, as in Claim 1, for use in personal care products that absorb body fluids (urine, menstrual fluid, human lactation, blood, wound exudates or perspiration).

27. A material as in Claim 1, for use in baby diapers, incontinence products, feminine hygiene products, nursing pad and the like.

28. A biocompatible, biodegradable, water-absorbent hybrid material, as in Claim 1, for use in paper making.

29. A biocompatible, biodegradable, water-absorbent hybrid material, as in Claim 1, for use in agriculture as soil conditioner.